

DESCRIPTION

TITLE OF INVENTION: CARBONATION ACCELERATOR FOR HYDRAULIC COMPOSITION AND METHOD FOR MANUFACTURING HYDRAULIC COMPOSITION HARDENED BODY

TECHNICAL FIELD

[0001] The present invention relates to a carbonation accelerator for a hydraulic composition and a method for manufacturing a hydraulic composition hardened body. More specifically, it relates to a carbonation accelerator for a hydraulic composition that can accelerate carbonation of the hydraulic composition when added thereto, and a method for manufacturing a hydraulic composition hardened body.

BACKGROUND ART

[0002] In recent years, efforts to achieve a decarbonized society, such as carbon-neutral or carbon-negative, have accelerated around the world. For example, Japan declared in 2020 the realization of "carbon-neutral by 2050", and in 2021, set a target of reducing greenhouse gas emissions by 46% in 2030 compared to 2013.

[0003] Accordingly, for example, the construction industry is also taking measures to reduce carbon dioxide (CO₂) emissions.

[0004] Specifically, concrete is a material that emits a

very large amount of carbon dioxide, since it is manufactured using cement, which emits a large amount of carbon dioxide in the manufacturing process. Therefore, in order to reduce carbon dioxide emissions, low-carbon cement and low-carbon concrete are known in which the used amount of cement is reduced by using industrial by-products such as blast furnace slag fine powder and fly ash.

[0005] In addition, precast concrete is also known that is obtained by hardening a concrete mixture of steelmaking slag powder and Portland cement to which $\gamma\text{-C}_2\text{S}$ has been added and subjecting the concrete to carbonation curing after demolding (see, for example, Patent Document 1). This precast concrete is based on technology in which carbonation due to the absorption of carbon dioxide proceeds at the surface of the concrete, resulting in densification in the surface region and thereby achieving high durability. The $\gamma\text{-C}_2\text{S}$ is $\gamma\text{-2CaO}\cdot\text{SiO}_2$ (sometimes called " γ -belite").

[0006] Here, in Patent Document 1, carbonation curing is carried out to densify the concrete and improve its durability. On the other hand, this technology is the fixation and absorption of carbon dioxide by concrete. That is, in the entire manufacturing process of the concrete, it can be said that the amount of carbon dioxide emission is reduced by an amount equivalent to the carbon dioxide fixed and absorbed in the concrete during carbonation curing. Thus, $\gamma\text{-C}_2\text{S}$ ($\gamma\text{-2CaO}\cdot\text{SiO}_2$) is sometimes used as a technology to reduce, fix,

or absorb carbon dioxide (CO₂).

[0007] Similarly, a carbonation accelerator that accelerates carbonation of alkaline earth metal compounds has been reported as one of the efforts to reduce greenhouse gas emissions (see Patent Document 2).

CITATION LIST

Patent Literature

[0008]

Patent Document 1: JP-A-2006-182583

Patent Document 2: JP-A-2023-103807

SUMMARY OF INVENTION

Technical Problem

[0009] However, there is still room for improvement in terms of the amount and rate of carbon dioxide absorption. Therefore, there is a demand for the development of a carbonation accelerator that can further increase the amount of carbon dioxide absorbed and fixed by concrete, improve the rate of carbon dioxide absorption, or achieve both. Increasing the amount of carbon dioxide absorbed by concrete at a given material age shortens the time required for a certain amount of carbon dioxide to be absorbed, and as a result, also shortens the carbonation curing period (shortens the manufacturing time of concrete products).

[0010] In view of the above circumstances, it is an object of the present invention to provide a carbonation accelerator for a hydraulic composition that can accelerate carbonation of the hydraulic composition when added thereto and can reduce the carbon dioxide balance of the hydraulic composition, and a method for manufacturing a hydraulic composition hardened body. The carbon dioxide balance is the amount of carbon dioxide calculated by the equation: "Amount of CO₂ derived from raw materials constituting concrete (i.e., amount of CO₂ generated in manufacturing of raw materials)" - "Amount of CO₂ absorbed and fixed by carbonation curing or the like". The expression "reduce the carbon dioxide balance" means increasing the amount of carbon dioxide reduction, that is, reducing the value of the amount of carbon dioxide calculated by the above equation.

Solution to Problem

[0011] As a result of intensive studies to solve the above problem, the present inventors have found that the above problem can be solved by containing a specific anionic surfactant. According to the present invention, the following carbonation accelerator for a hydraulic composition and a method of manufacturing a hydraulic composition hardened body are provided.

[0012] [1] A carbonation accelerator for a hydraulic composition comprising an anionic surfactant at a ratio of 10

to 100% by mass, wherein the anionic surfactant is a compound containing an organic acid ion with a hydrophobic group having 6 to 50 carbon atoms in the molecule.

[0013] [2] The carbonation accelerator for a hydraulic composition according to [1], wherein the anionic surfactant is at least one compound selected from the compounds represented by the following general formula (1).

[0014]

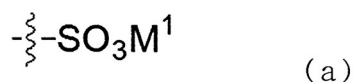
[Formula 1]



(In the general formula (1), R^1 is an alkyl group having 1 to 24 carbon atoms, an alkenyl group having 2 to 24 carbon atoms, an aryl group having 8 to 20 carbon atoms, a residue obtained by removing a carboxylic acid from rosin, or a residue obtained by removing hydrogen from an adduct formed by adding a total of 1 to 10 moles of an alkylene oxide having 2 to 3 carbon atoms to 1 mole of an aliphatic alcohol having 1 to 24 carbon atoms. X is represented by the following general formulas (a) to (f).)

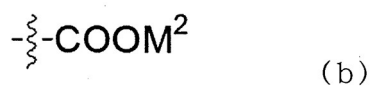
[0015]

[Formula 2]



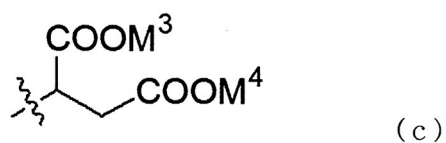
[0016]

[Formula 3]



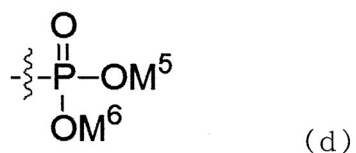
[0017]

[Formula 4]



[0018]

[Formula 5]



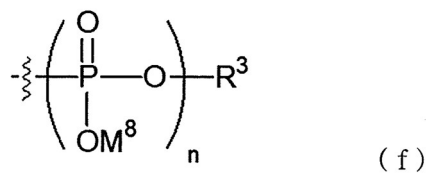
[0019]

[Formula 6]



[0020]

[Formula 7]



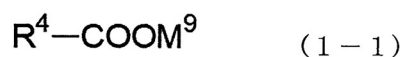
(In the general formulas (a) to (f), R^2 and R^3 are each independently a residue obtained by removing a hydroxyl group from an aliphatic alcohol having 1 to 24 carbon atoms, or a residue obtained by removing a hydroxyl group from an adduct

formed by adding a total of 1 to 10 moles of an alkylene oxide having 2 to 3 carbon atoms to 1 mole of an aliphatic alcohol having 1 to 24 carbon atoms. M^1 to M^8 are each independently an alkali metal, an alkaline earth metal, ammonium, or an organic amine. n is an integer of 2 or 3.)

[0021] [3] The carbonation accelerator for a hydraulic composition according to [1], wherein the anionic surfactant is at least one selected from the compounds represented by the following general formulas (1-1) to (1-5).

[0022]

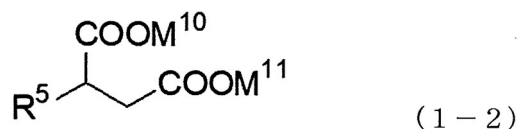
[Formula 8]



(In the general formula (1-1), R^4 is an alkyl group having 6 to 20 carbon atoms, an alkenyl group having 6 to 20 carbon atoms, or an acyl residue of rosin. M^9 is hydrogen, an alkali metal, an alkaline earth metal, ammonium, or an organic amine.)

[0023]

[Formula 9]

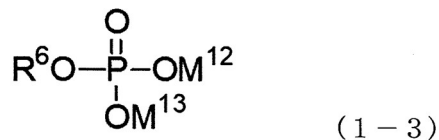


(In the general formula (1-2), R^5 is an alkyl group having 6 to 20 carbon atoms, an alkenyl group having 6 to 20 carbon atoms, or an aryl group having 6 to 20 carbon atoms. M^{10} to M^{11} are hydrogen, an alkali metal, an alkaline earth metal,

ammonium, or an organic amine.)

[0024]

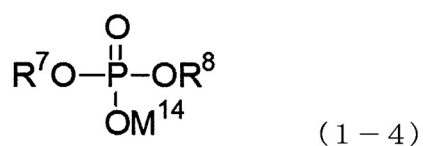
[Formula 10]



(In the general formula (1-3), R^6 is a residue obtained by removing a hydroxyl group from an aliphatic alcohol having 6 to 20 carbon atoms, or a residue obtained by removing a hydroxyl group from an adduct formed by adding a total of 1 to 10 moles of an alkylene oxide having 2 to 3 carbon atoms to 1 mole of an aliphatic alcohol having 6 to 20 carbon atoms. M^{12} and M^{13} are each independently hydrogen, an alkali metal, an alkaline earth metal, ammonium or an organic amine.)

[0025]

[Formula 11]

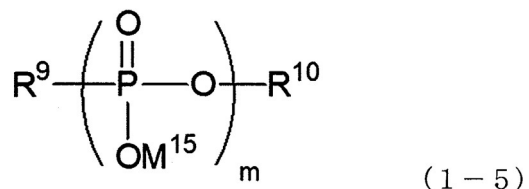


(In the general formula (1-4), R^7 and R^8 are each independently a residue obtained by removing a hydroxyl group from an aliphatic alcohol having 6 to 20 carbon atoms, or a residue obtained by removing a hydroxyl group from an adduct formed by adding a total of 1 to 10 moles of an alkylene oxide having 2 to 3 carbon atoms to 1 mole of an aliphatic alcohol having 6 to 20 carbon atoms. M^{14} is hydrogen, an alkali metal, an

alkaline earth metal, ammonium or an organic amine.)

[0026]

[Formula 12]



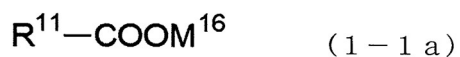
(In the general formula (1-5), R^9 and R^{10} are each independently a residue obtained by removing a hydroxyl group from an aliphatic alcohol having 6 to 20 carbon atoms, or a residue obtained by removing a hydroxyl group from an adduct formed by adding a total of 1 to 10 moles of an alkylene oxide having 2 to 3 carbon atoms to 1 mole of an aliphatic alcohol having 6 to 20 carbon atoms. M^{15} is hydrogen, an alkali metal, an alkaline earth metal, ammonium or an organic amine. m is an integer of 2 or 3.)

[0027]

[4] The carbonation accelerator for a hydraulic composition according to [3], wherein the compound represented by the general formula (1-1) is a compound represented by the following general formula (1-1a), and the anionic surfactant is a mixture containing at least one selected from the compound represented by the general formula (1-1a) and the compound represented by the general formulas (1-2) to (1-5).

[0028]

[Formula 13]



(In the general formula (1-1a), R^{11} is an alkyl group having 6 to 20 carbon atoms or an alkenyl group having 6 to 20 carbon atoms. M^{16} is hydrogen, an alkali metal, an alkaline earth metal, or an organic amine.)

[0029] [5] The carbonation accelerator for a hydraulic composition according to any one of [1] to [4], which is added to a hydraulic composition that becomes a hydraulic composition hardened body through a carbonation curing step, which is a step of curing in an environment with a carbon dioxide volume concentration of 5% or more.

[0030] [6] The carbonation accelerator for a hydraulic composition according to any one of [1] to [4], which is added to a hydraulic composition containing a binder that contains blast furnace slag fine powder at 40 to 99% by mass, water, and an aggregate.

[0031] [7] The carbonation accelerator for a hydraulic composition according to any one of [1] to [4], wherein the hydraulic composition contains γ - $2CaO \cdot SiO_2$.

[0032] [8] The carbonation accelerator for a hydraulic composition according to any one of [1] to [4], wherein the hydraulic composition contains at least one selected from the following CO_2 -fixed fine powder and the following CO_2 -fixed modified recycled fine aggregate.

CO_2 -fixed fine powder: including modified concrete powder, which has a 50% particle size of 50 μm or less and is a reaction product of recycled concrete powder and carbon dioxide gas,

wherein the modified concrete powder contains calcium carbonate and a siliceous material, wherein the content ratio of the CO₂-fixed fine powder in the hydraulic composition is in the range of 1 to 100% by mass with respect to 100% by mass of the binder.

CO₂-fixed modified recycled fine aggregate: including modified recycled fine aggregate in which all particles have a particle size of 10 mm or less and 85% or more of the particles have a particle size of 5 mm or less, the modified recycled fine aggregate being a dry or wet reaction product of recycled fine aggregate having a water absorption greater than 3.0% and 10% or less and carbon dioxide gas, wherein the modified recycled fine aggregate contains calcium carbonate and silicon dioxide, wherein the content ratio of the CO₂-fixed modified recycled fine aggregate in the hydraulic composition is in the range of 10 to 100% by volume with respect to the total aggregate volume.

[0033] [9] A method for manufacturing a hydraulic composition hardened body, comprising: a preparation step of preparing a hydraulic composition containing a carbonation accelerator for a hydraulic composition according to any one of [1] to [4], a binder containing blast furnace slag fine powder at 40 to 99% by mass, and water; a hardening step of hardening the obtained hydraulic composition to obtain a hydraulic composition hardened body, and a carbonation curing step of curing the obtained hydraulic composition hardened

body in an environment with a carbon dioxide volume concentration of 5% or more to absorb and fix carbon dioxide in the hydraulic composition hardened body.

Effects of the Invention

[0034] The carbonation accelerator for a hydraulic composition of the present invention exhibits an effect that, by being added to a hydraulic composition, it accelerates the carbonation of the hydraulic composition and can reduce the carbon dioxide balance of the hydraulic composition.

[0035] According to the method for manufacturing a hydraulic composition hardened body of the present invention, since a hydraulic composition containing the carbonation accelerator for a hydraulic composition of the present invention is used, it is possible to increase the amount of carbon dioxide reduced in the manufacturing process.

DESCRIPTION OF EMBODIMENTS

[0036] Hereinafter, embodiments of the present invention will be described. However, the present invention is not limited to the following embodiments. Therefore, it should be understood that modifications, improvements, and the like may be made to the following embodiments as appropriate based on the ordinary knowledge of a person skilled in the art without departing from the spirit of the present invention. In the following examples and the like, unless otherwise stated, %

means % by mass and part means part by mass.

[0037] (1) Carbonation accelerator for hydraulic composition:

The carbonation accelerator for a hydraulic composition of the present invention contains an anionic surfactant at a ratio of 10 to 100% by mass, wherein the anionic surfactant is a compound containing an organic acid ion with a hydrophobic group having 6 to 50 carbon atoms in the molecule.

[0038] In such a carbonation accelerator for a hydraulic composition, by being added to a hydraulic composition, it can accelerate carbonation of the hydraulic composition and increase the amount of carbon dioxide absorbed by the hydraulic composition (i.e., the amount of carbon dioxide reduction). In other words, the carbon dioxide balance of the hydraulic composition can be reduced. By hydration of cement, calcium silicate hydrate (C-S-H), calcium hydroxide (CH), and the like are formed. In addition, in the hydraulic composition, calcium oxide (CaO) and the like are contained as components derived from the raw materials. Then, carbon dioxide can be absorbed and fixed in the hydraulic composition (the hardened body of the hydraulic composition) by carbonation (reaction with carbon dioxide) of these compounds.

[0039] Thermal power plants, for example, release carbon dioxide into the atmosphere as exhaust gas. The carbon dioxide is considered to be one of the causes of global warming; however, by supplying carbon dioxide in exhaust gas to a

carbonation curing step, the carbon dioxide can be absorbed into a hydraulic composition, thereby enabling a reduction in carbon dioxide. The hardened body of the hydraulic composition can fix carbon dioxide in the atmosphere not only during the carbonation curing step but also over a long period of time after being installed at a predetermined location after the step.

[0040] (1-1) Anionic surfactant:

The anionic surfactant has a content ratio of 10 to 100% by mass, preferably 15 to 100% by mass, and more preferably 20 to 100% by mass. By setting the ratio within the above range, the carbon dioxide balance of the hydraulic composition can be reduced.

[0041] In addition, the "component other than anionic surfactant" shall also reduce the content ratio in the following points. First, if the "component other than anionic surfactant" is other than water, it is possible to avoid adding too much of the "component other than anionic surfactant" when the carbonation accelerator for a hydraulic composition is added to the hydraulic composition. As a result, it is possible to minimize concerns that the "component other than anionic surfactant" may affect various physical properties of the hydraulic composition. If the "component other than anionic surfactant" is water (i.e., aqueous anionic surfactant solution), the above content ratio makes it easier to maintain the product stability of the carbonation accelerator for a

hydraulic composition. Therefore, if the water content is too high, it is likely to cause the occurrence of deterioration such as putrefaction.

[0042] An anionic surfactant is a compound containing an organic acid ion with a hydrophobic group having 6 to 50 carbon atoms in the molecule, and the particular organic acid ion can increase the amount of carbon dioxide absorbed by the hardened body of the hydraulic composition.

[0043] By containing the above specific anionic surfactant in the carbonation accelerator for a hydraulic composition, the following can be inferred. That is, fine air bubbles can be uniformly entrained in a hydraulic composition containing a carbonation accelerator for a hydraulic composition. This improves material permeability when the hydraulic composition is hardened, and as a result, a flow path for a gas (carbon dioxide) to flow from the outer surface toward the center is favorably formed. The formation of the flow path facilitates the flow of carbon dioxide to the center of the hardened body during the carbonation curing of the hardened body of the hydraulic composition, thereby further accelerating carbonation.

[0044] (1-1-1) Compound represented by general formula (1):

The anionic surfactant is not particularly limited as long as it satisfies the above conditions; however, it is preferably at least one compound selected from the compounds

represented by the following general formula (1). That is, it may be a single compound that corresponds to the compound represented by the general formula (1), or a combination of two or more compounds that correspond to the compound represented by the general formula (1).

[0045]

[Formula 14]



(In the general formula (1), R^1 is an alkyl group having 1 to 24 carbon atoms, an alkenyl group having 2 to 24 carbon atoms, an aryl group having 8 to 20 carbon atoms, a residue obtained by removing a carboxylic acid from rosin, or a residue obtained by removing hydrogen from an adduct formed by adding a total of 1 to 10 moles of an alkylene oxide having 2 to 3 carbon atoms to 1 mole of an aliphatic alcohol having 1 to 24 carbon atoms. X is represented by the general formulas (a) to (f) above.)

[0046] Rosin contains a diterpene acid-based compound referred to as resin acids (rosin acid). The resin acids contained in rosin are mainly abietic acid; however, in addition to the abietic acid, examples thereof include neoabietic acid, dehydroabietic acid, tetrahydroabietic acid, palastrinic acid, pimaric acid, isopimaric acid, sandalacopimaric acid, and levopimaric acid.

[0047] The "residue obtained by removing a carboxylic acid

from rosin" in R^1 in the general formula (1) is a residue obtained by removing a carboxylic acid from resin acid constituting rosin. That is, for example, a residue obtained by removing carboxylic acid from abietic acid and a residue obtained by removing carboxylic acid from palustric acid. Thus, the "residue obtained by removing a carboxylic acid from rosin" usually includes two or more "residues obtained by removing a carboxylic acid from rosin", but may be a single residue (e.g., a residue obtained by removing a carboxylic acid from abietic acid).

[0048] The same applies to the rosin of the acyl residue of rosin in R^4 in the general formula (1-1). The "acyl residue of rosin" is an acyl residue of carboxylic acids such as resin acids constituting rosin.

[0049] (1-1-2) Compounds represented by general formulas (1-1) to (1-5):

More specifically, among the compounds represented by the general formula (1), the anionic surfactant is more preferably at least one selected from the compounds represented by the above general formulas (1-1) to (1-5). By containing these compounds, the amount of carbon dioxide absorbed by a hardened body of the hydraulic composition can be further increased.

[0050] For the compounds represented by the general formulas (1-3) to (1-5), the anionic surfactant can be constituted as a mixture of these compounds. The compositional

ratios thereof can be determined by measuring P-nuclear NMR integral ratio.

[0051] The method for measuring the P-nuclear NMR integral ratio is shown below. First, an excess amount of KOH is added to the mixture of compounds represented by the general formulas (1-3) to (1-5) (phosphate esters) to adjust the pH to 12 or higher. Next, ^{31}P -NMR measurement is performed under these conditions (that is, conditions in which an alkaline excess-neutralization pretreatment with KOH has been carried out), and a P-nuclear NMR integral ratio can be calculated based on the following equations (a) to (c) using the obtained measurement values. The ^{31}P -NMR is specifically a MERCURY plus NMR Spectrometer System (300 MHz), which is a product manufactured by Varian, Inc. The solvent used in the ^{31}P -NMR measurement can be a mixed solvent of heavy water/tetrahydrofuran = 8/2 (volume ratio).

[0052]

[Equation 1]

$$\begin{array}{l} \text{P-nuclear NMR integral ratio (\%)} \\ \text{of Compound (phosphate ester)} \\ \text{represented by general formula} \\ \text{(1-3)} \end{array} = \frac{\text{P-formula 1}}{(\text{P-formula 1} + \text{P-formula 2} + \text{P-formula 3})} \times 100 \quad (\text{a})$$

[0053]

[Equation 2]

$$\begin{array}{l} \text{P-nuclear NMR integral ratio (\%)} \\ \text{of Compound (phosphate ester)} \\ \text{represented by general formula} \\ \text{(1-4)} \end{array} = \frac{\text{P-formula 2}}{(\text{P-formula 1} + \text{P-formula 2} + \text{P-formula 3})} \times 100 \quad (\text{b})$$

[0054]

[Equation 3]

$$\begin{array}{l} \text{P-nuclear NMR integral ratio (\%)} \\ \text{of Compound (phosphate ester)} \\ \text{represented by general formula} \\ \text{(1-5)} \end{array} = \frac{\text{P-formula 3}}{(\text{P-formula 1} + \text{P-formula 2} + \text{P-formula 3})} \times 100 \quad (\text{c})$$

[0055] In the above equations (a) to (c), P-formula 1, P-formula 2, and P-formula 3 are as follows.

P-formula 1: P-nuclear NMR integral value attributed to the compound (phosphate ester) represented by the general formula (1-3).

P-formula 2: P-nuclear NMR integral value attributed to the compound (phosphate ester) represented by the general formula (1-4).

P-formula 3: P-nuclear NMR integral value attributed to the compound (phosphate ester) represented by the general formula (1-5).

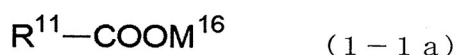
[0056] The "alkaline excess-neutralization pretreatment" means a pretreatment in which an excess amount of alkali is added to a phosphate ester. In the ^{31}P -NMR measurement, the "alkaline excess-neutralization pretreatment" clearly separates the peaks attributed to phosphate esters, allowing the calculation of the P-nuclear NMR integral ratio attributed to each compound according to the following equations (a) to (c).

[0057] (1-1-3) Compound represented by general formula (1-1a):

The compound represented by the general formula (1-1) is preferably a compound represented by the following general formula (1-1a). In the present invention, the anionic surfactant is preferably a mixture containing a compound represented by the following general formula (1-1a) and at least one compound selected from the compounds represented by the general formulas (1-2) to (1-5). By containing these compounds, the amount of carbon dioxide absorbed by a hardened body of the hydraulic composition can be further increased.

[0058]

[Formula 15]



(In the general formula (1-1a), R^{11} is an alkyl group having 6 to 20 carbon atoms or an alkenyl group having 6 to 20 carbon atoms. M^{16} is hydrogen, an alkali metal, an alkaline earth metal, or an organic amine.)

[0059] R^{11} in the general formula (1-1a) is an alkyl group having 6 to 20 carbon atoms or an alkenyl group having 6 to 20 carbon atoms.

[0060] M^{16} in the general formula (1-1a) is hydrogen, an alkali metal, an alkaline earth metal, or an organic amine.

[0061] (1-2) Other components:

The carbonation accelerator for a hydraulic composition of the present invention may contain other components in addition to the above-described anionic surfactant within a

range in which the effect is not impaired.

[0062] As other components, for example, water and additives conventionally known to be added to hydraulic compositions can be selected and employed as appropriate.

[0063] The other components may be used singly, or two or more thereof may be used in combination.

[0064] The carbonation accelerator for a hydraulic composition of the present invention is preferably added to the hydraulic composition described below.

[0065] (2) Hydraulic composition:

The carbonation accelerator for a hydraulic composition of the present invention can be added to a hydraulic composition. The hydraulic composition may include, similar to the conventionally known hydraulic compositions, a binder (hydraulic binder), water, and aggregates (fine aggregate and coarse aggregate).

[0066] The content ratio of the carbonation accelerator for a hydraulic composition of the present invention in the hydraulic composition is not particularly limited and can be appropriately set. For example, the content ratio of the carbonation accelerator for a hydraulic composition of the present invention can be 0.0005 to 2% by mass with respect to 100% by mass of the binder.

[0067] Examples of the binder include various Portland cements such as ordinary Portland cement, moderate-heat Portland cement, low-heat Portland cement, high-early strength

Portland cement, and sulfate resisting Portland cement, various cements such as blast furnace cement, fly ash cement, and silica fume cement.

[0068] Further, as a binder, various admixtures such as fly ash, blast furnace slag fine powder, limestone fine powder, stone powder, silica fume, expansive material, anhydrous gypsum, hemihydrate gypsum, and dihydrate gypsum may be used in combination with the various cements described above.

[0069] The binder preferably contains blast furnace slag fine powder at 40 to 99% by mass. That is, the hydraulic composition to which the carbonation accelerator for a hydraulic composition of the present invention is added should contain a binder containing blast furnace slag fine powder at 40 to 99% by mass, water, and aggregates. The content ratio of the blast furnace slag fine powder is preferably 50 to 99% by mass, and more preferably 60 to 99% by mass. In this manner, the carbon dioxide balance of the hydraulic composition can be further reduced.

[0070] Examples of the aggregate include fine aggregate and coarse aggregate.

[0071] Examples of the fine aggregate include river sand, mountain sand, land sand, sea sand, silica sand, crushed sand, various types of slag fine aggregates, and various types of recycled fine aggregates, but may also include fine particulate components such as clay.

[0072] Examples of the coarse aggregate include river

gravel, mountain gravel, land gravel, crushed stone, various types of slag coarse aggregates, lightweight aggregate, and various types of recycled coarse aggregates.

[0073] The hydraulic composition preferably contains γ - $2\text{CaO}\cdot\text{SiO}_2$. That is, the carbonation accelerator for a hydraulic composition of the present invention is preferably added to a hydraulic composition containing γ - $2\text{CaO}\cdot\text{SiO}_2$. In this manner, γ - $2\text{CaO}\cdot\text{SiO}_2$ exerts a function of fixing carbon dioxide, thereby making it possible to further increase the amount of carbon dioxide absorbed by the hardened body of the hydraulic composition (i.e., the amount of carbon dioxide reduction). As a result, the carbon dioxide balance of the hydraulic composition can be further reduced. The γ - $2\text{CaO}\cdot\text{SiO}_2$ is a material that hardens by carbonation. The γ - $2\text{CaO}\cdot\text{SiO}_2$ may be added to a hydraulic composition containing a binder that contains blast furnace slag fine powder at 40 to 99% by mass, water, and aggregates, or to a hydraulic composition that do not contain such a binder and the like.

[0074] The content ratio of γ - $2\text{CaO}\cdot\text{SiO}_2$ is not particularly limited; however, for example, it may be a ratio equivalent to 1 to 30% by mass on an internal basis with respect to 100% by mass of the binder.

[0075] The hydraulic composition preferably includes at least one selected from the following CO_2 -fixed fine powder and the following CO_2 -fixed modified recycled fine aggregate. In this manner, the carbon dioxide balance of the hydraulic

composition can be further reduced. Carbon Capture and Utilization (CCU) materials such as CO₂-fixed fine powder and CO₂-fixed modified recycled aggregate (including CO₂-fixed modified recycled fine aggregate) are powders and aggregates produced by previously reacting CO₂ with calcium components derived from waste materials such as waste concrete. The CCU material may be used for carbon neutral or carbon negative concrete. Incidentally, in the hydraulic composition, CO₂-fixed modified recycled coarse aggregate may further be used in addition to CO₂-fixed modified recycled fine aggregate, or CO₂-fixed modified recycled coarse aggregate may be used instead of CO₂-fixed modified fine aggregate.

[0076] (CO₂-fixed fine powder)

The CO₂-fixed fine powder contains modified concrete powder, which has a 50% particle size of 50μm or less and is a reaction product of recycled concrete powder and carbon dioxide gas, and the modified concrete powder contains calcium carbonate and a siliceous material. The content ratio of the CO₂-fixed fine powder is in the range of 1 to 100% by mass with respect to 100% by mass of the binder.

[0077] The CO₂-fixed fine powder can be produced as follows. That is, a concrete mass is first crushed or grinded to recover recycled concrete fine powder with a median diameter of 100μm or less. The method of performing the crushing or grinding is not particularly limited, and known crushing or grinding devices such as a shot-blast-type crushing device, an

impact crusher, and a grinding device of a mechanical rubbing and grinding type that does not involve heating can be used. Next, the recovered recycled concrete fine powder is reacted with carbon dioxide gas with a volume concentration of 5% or more to fix CO₂ to the cement-derived components in the recycled concrete fine powder. The reaction with carbon dioxide gas can be either a dry method in which gaseous carbon dioxide gas is brought into contact, or a wet method in which the recycled concrete fine powder is immersed in a solution such as water, and then carbon dioxide gas is blown into the liquid (dispersion liquid). In this way, CO₂-fixed fine powder can be produced.

[0078] (CO₂-fixed modified recycled aggregate)

The CO₂-fixed modified recycled aggregate is an aggregate produced by previously reacting CO₂ with calcium components derived from waste materials such as waste concrete, and examples thereof include CO₂-fixed modified recycled fine aggregate and CO₂-fixed modified recycled coarse aggregate. Of these, the use of CO₂-fixed modified recycled fine aggregate is preferable. This is because the CO₂-fixed modified recycled fine aggregate contains more calcium components derived from cements, fixes a larger amount of CO₂ during the production of the CO₂-fixed modified recycled aggregate (that is, the "amount of material-derived carbon dioxide emission" is smaller), and is more effective in reducing the carbon dioxide balance when applied to a hydraulic composition.

[0079] (CO₂-fixed modified recycled fine aggregate)

The CO₂-fixed modified recycled fine aggregate includes modified recycled fine aggregate in which all particles have a particle size of 10 mm or less and 85% or more of the particles have a particle size of 5 mm or less, and the modified recycled fine aggregate is a dry or wet reaction product of recycled fine aggregate having a water absorption of greater than 3.0% and 10% or less and carbon dioxide gas. The modified recycled fine aggregate contains calcium carbonate and silicon dioxide. The content ratio of the CO₂-fixed modified recycled fine aggregate is in the range of 10 to 100% by volume with respect to the total aggregate volume.

[0080] The CO₂-fixed modified recycled fine aggregate can be produced as follows. That is, a concrete mass is first crushed or grinded to obtain recycled fine aggregate. The method of performing the crushing or grinding is not particularly limited, and known crushing or grinding devices such as a shot-blast-type crushing device, an impact crusher, and a grinding device of a mechanical rubbing and grinding type that does not involve heating can be used. Then, particles are classified so that all particles have a particle size of 10 mm or less, and among these, particles with a water absorption more than 3% and 10% or less are used as recycled fine aggregate. The recycled fine aggregate is then reacted with carbon dioxide gas with a volume concentration of 5% or more to produce CO₂-fixed modified recycled fine aggregate

containing calcium carbonate and silicon dioxide. The reaction of recycled fine aggregate with carbon dioxide gas may employ a dry method or a wet method. In this way, CO₂-fixed modified recycled fine aggregate can be produced.

[0081] The content ratio of the CO₂-fixed fine powder can be 1 to 100% by mass, preferably 10 to 90% by mass, and even more preferably 30 to 80% by mass, with respect to 100% by mass of the binder as described above.

[0082] The content ratio of the CO₂-fixed modified recycled fine aggregate can be 10 to 100% by volume, preferably 20 to 100% by volume, and even more preferably 30 to 100% by volume, with respect to the total aggregate volume (more specifically, the aggregate volume using natural aggregates of the original mix) as described above.

[0083] Here, the original mix refers to a mix without CO₂-fixed modified recycled fine aggregate. Further, natural aggregates refer to aggregates that have not been subjected to CO₂ fixation treatment. Examples of the natural aggregates include, in the case of fine aggregates, river sand, mountain sand, land sand, sea sand, silica sand, crushed sand, and various types of slag fine aggregates, and in the case of coarse aggregates, river gravel, mountain gravel, land gravel, crushed stone, various types of slag coarse aggregates, and lightweight aggregates. That is, "with respect to the aggregate volume using natural aggregates of the original mix" means "with respect to the volume of natural aggregates such as river

sand as it has been used in the past". In other words, CO₂-fixed modified recycled fine aggregate may be used in place of aggregates conventionally used as aggregates (100% by volume) or may be used by replacing about 1/5 (i.e., 20% by volume) thereof.

[0084] The hydraulic composition may further contain other constituents as appropriate within a range in which the effect is not impaired. Examples of such other components include a saccharide, a coagulation retardation component made of an oxycarboxylic acid or the like, a component having a dispersing action made of sodium lignin sulfonate or the like, a defoaming agent made of an oxyalkylene-based compound or the like, a curing accelerator made of an alkanolamine or the like, a shrinkage reducing agent made of a polyoxyalkylene alkyl ether or the like, a thickener made of a cellulose ether-based compound or the like, a preservative made of an isothiazoline-based compound or the like, and a rust inhibitor made of a nitrite or the like.

[0085] The content ratio of the other components can be, for example, 0 to 5% by mass with respect to 100% by mass of the binder.

[0086] The hydraulic composition may employ any conventionally known ratio as a ratio of water to binder (water/binder ratio) as appropriate; for example, it may be 25 to 70% by mass.

[0087] The hydraulic composition can be hardened to form

a hydraulic composition hardened body (specifically, mortar and concrete). When obtaining the hydraulic composition hardened body in this manner, it is preferable to carry out a carbonation curing step, which is the step of curing in an environment with a carbon dioxide volume concentration of 5% or more. By carrying out the carbonation curing step in this manner, a large amount of carbon dioxide can be absorbed and fixed in the hydraulic composition (hydraulic composition hardened body).

[0088] The volume concentration of carbon dioxide in the carbonation curing step is not particularly limited, but can usually be 5 to 100%.

[0089] (3) Method for manufacturing hydraulic composition hardened body:

The method for manufacturing a hydraulic composition hardened body of the present invention includes the following steps: a preparation step of preparing a hydraulic composition containing at least a carbonation accelerator for a hydraulic composition of the present invention, a binder containing blast furnace slag fine powder at 40 to 99% by mass, and water; a hardening step of hardening the obtained hydraulic composition to obtain a hydraulic composition hardened body; and a carbonation curing step of curing the obtained hydraulic composition hardened body in an environment with a carbon dioxide volume concentration of 5% or more to absorb and fix carbon dioxide in the hydraulic composition hardened body.

According to the method for manufacturing a hydraulic composition hardened body, since a hydraulic composition containing the carbonation accelerator for a hydraulic composition of the present invention is used, the amount of carbon dioxide reduced in the manufacturing process is increased.

[0090] (3-1) Preparation step:

The preparation step is a step of preparing a hydraulic composition containing at least a carbonation accelerator for a hydraulic composition of the present invention, a binder containing blast furnace slag fine powder at 40 to 99% by mass, and water.

[0091] As described above, blast furnace slag fine powder is contained at 40 to 99% by mass, preferably 50 to 99% by mass, and more preferably 60 to 99% by mass. The above content ratio increases the amount of carbon dioxide reduced in the manufacturing process of the hydraulic composition hardened body.

[0092] (3-2) Hardening step:

The hardening step is a step of hardening the hydraulic composition obtained in the preparation step to obtain a hydraulic composition hardened body. Conventional known methods for hardening a hydraulic composition can be employed as appropriate.

[0093] (3-3) Carbonation curing step:

The carbonation curing step is a step of curing the

hydraulic composition hardened body obtained in the hardening step in an environment with a carbon dioxide volume concentration of 5% or more (carbonation curing) to absorb and fix carbon dioxide in the hydraulic composition hardened body.

[0094] In this step, carbon dioxide in the atmosphere is absorbed into the hydraulic composition hardened body and carbonated and fixed. By using the carbonation accelerator for a hydraulic composition of the present invention, the following may be inferred. That is, fine air bubbles are uniformly entrained in the hydraulic composition. Therefore, in the hydraulic composition hardened body, a flow path for a gas (carbon dioxide) to flow from the outer surface toward the center is favorably formed. The formation of the flow path facilitates the flow of carbon dioxide to the center of the hydraulic composition hardened body, allowing more carbon dioxide to be absorbed and fixed in the hydraulic composition (hydraulic composition hardened body).

[0095] The volume concentration of carbon dioxide is not particularly limited, but can usually be 5 to 100%.

[0096] If the volume concentration of carbon dioxide is less than 5%, the available amount of carbon dioxide present for absorption is too small, which may result in a prolonged carbonation curing period before reaching a predetermined amount of carbon dioxide fixation.

Examples

[0097] Hereinafter, the present invention will be described in detail based on examples, but the present invention is not limited to these examples.

[0098] (Examples 1 to 48, Comparative Examples 1 to 12)

(1) Carbonation accelerator for hydraulic composition:

First, carbonation accelerators for a hydraulic composition A-1 to A-16 and RA-1 to RA-2 in Examples and Comparative Examples were prepared in the formulations shown in Table 1 below.

[0099] [Table 1]

Notation	Carbonation accelerator for a hydraulic composition										Total amount of essential constituent components (% by mass)	Concentration of carbonation accelerator for a hydraulic composition (%)
	Essential constituent components (anionic surfactant)						Other components					
	First component		Second component		Third component							
	Type	(% by mass)	Type	(% by mass)	Type	(% by mass)	Type	(% by mass)	Type	(% by mass)		
A-1	a-1	19.6	a-2	10.7	-	-	-	b-1	69.6	30.4	10.0	
A-2	a-3	75.0	a-9	25.0	-	-	-	-	-	100.0	10.0	
A-3	a-4	100.0	-	-	-	-	-	-	-	100.0	10.0	
A-4	a-5	18.9	a-6-1	15.0	-	-	-	b-2	66.1	33.9	10.0	
A-5	a-6-2	40.0	a-10	40.0	a-13	20.0	-	-	-	100.0	10.0	
A-6	a-6-2	40.0	a-10	40.0	a-17	20.0	-	-	-	100.0	10.0	
A-7	a-6-2	40.0	a-11	40.0	a-18	20.0	-	-	-	100.0	10.0	
A-8	a-7	80.0	-	-	-	-	-	b-3	20.0	80.0	10.0	
A-9	a-8	100.0	-	-	-	-	-	-	-	100.0	10.0	
A-10	a-9	33.3	-	-	-	-	-	b-4	66.7	33.3	10.0	
A-11	a-10	100.0	-	-	-	-	-	-	-	100.0	10.0	
A-12	a-1	16.0	-	-	-	-	-	b-2	84.0	16.0	10.0	
A-13	a-12	100.0	-	-	-	-	-	-	-	100.0	10.0	
A-14	a-1	11.0	-	-	-	-	-	b-2	89.0	11.0	10.0	
A-15	a-14	100.0	-	-	-	-	-	-	-	100.0	10.0	
A-16	a-15	43.3	a-16	56.7	-	-	-	-	-	100.0	10.0	
RA-1	a-15	8.0	-	-	-	-	-	b-1	92.0	8.0	10.0	
RA-2	-	-	-	-	-	-	-	b-5	100.0	0.0	10.0	

[0100] Next, Table 2 below specifically shows each of the essential constituent components (anionic surfactants a-1 to

a-18) and other components (b-1 to b-5) shown in Table 1. b-5 is a product manufactured by Kao Corporation under the name "Skish 21B" (special polycarboxylic acid type surfactant).

[0101] [Table 2]

Notation	R1-	Component	Molecular weight	P-nuclear NMR integral ratio (%)		
				mono	di	poly
a-1	C18 alkenyl	oleic acid	282.5	-	-	-
a-2	C18 alkenyl	potassium oleate	320.6	-	-	-
a-3	C12 alkyl	sodium laurate	222.3	-	-	-
a-4	C18 alkyl	potassium stearate	322.6	-	-	-
a-5	C8 alkyl	octyl alcohol phosphate ester	227.2	56	32	12
a-6-1	C8 alkyl	potassium salt of octyl alcohol phosphate ester	265.3	56	32	12
a-6-2	C8 alkyl	potassium salt of octyl alcohol phosphate ester	265.3	88	10	2
a-7	C8 branched alkyl	2-ethylhexyl alcohol phosphate ester	227.2	81	16	3
a-8	C8 alkyl-EO5	octyl alcohol EO5mol adduct phosphate ester	446.2	81	16	3
a-9	C9 alkyl	potassium salt of nonyl alcohol phosphate ester	263.3	62	25	13
a-10	C12 alkenyl	dipotassium dodecenyl succinate	360.6	-	-	-
a-11	C8 alkenyl	sodium octenyl succinate	250.3	-	-	-
a-12	rosin	potassium salt of gum rosin	373.0	-	-	-
a-13	C12 branched alkyl	branched sodium dodecylbenzenesulfonate	348.1	-	-	-
a-14	C12 alkyl	linear sodium dodecylbenzenesulfonate	348.1	-	-	-
a-15	C10 alkyl	sodium decyl sulfate	260.3	-	-	-
a-16	C12 alkyl-EO2	sodium higher alcohol ethoxysulfate	351.1	-	-	-
a-17	C14 alkenyl	tetradecenesulfonate (sodium α -olefin sulfonate)	298.1	-	-	-
a-18	C14-17 alkyl	sodium sec-alkyl (C14-17) sulfonate	289.1	-	-	-
b-1	-	lauryl amine EO20mol adduct	1063.4	-	-	-
b-2	-	stearyl amine EO18mol adduct	1059.5	-	-	-
b-3	-	butyl diglycol	162.2	-	-	-
b-4	-	butyl triglycol	206.3	-	-	-
b-5	-	special polycarboxylic acid type surfactant	12000	-	-	-

[0102] The production method of each anionic surfactant (a-1 to a-18) is specifically described below.

[0103] The anionic surfactant (a-1) used was oleic acid from Tokyo Chemical Industry Co., Ltd. The anionic surfactant (a-13) used was branched sodium dodecylbenzenesulfonate from Tokyo Chemical Industry Co., Ltd. The anionic surfactant (a-14) used was linear sodium dodecylbenzenesulfonate from Tokyo Chemical Industry Co., Ltd. The anionic surfactant (a-15) used was sodium decyl sulfate from Kao Corporation. The anionic surfactant (a-16) used was sodium higher alcohol ethoxysulfate from TAYCA Co., Ltd. The anionic surfactant (a-17) used was sodium tetradecenesulfonate (sodium α -olefin sulfonate) from Lion Specialty Chemicals Co., Ltd. The anionic surfactant (a-18) used was sodium sec-alkyl (C14-17) sulfonate from Clariant.

[0104] The anionic surfactants (a-1 to a-12) are classified according to which of the compounds represented by the general formulas (1-1) to (1-5) they correspond to, as follows. The anionic surfactants a-1 to a-4 and a-12 correspond to the compound represented by the general formula (1-1), and the anionic surfactants a-10 to a-11 correspond to the compound represented by the general formula (1-2). The anionic surfactants a-5 to a-9 are mixtures of the compounds represented by the general formulas (1-3) to (1-5). The anionic surfactants a-13 to a-18 are compounds containing an organic acid ion with a hydrophobic group having 6 to 50 carbon atoms in the molecule.

[0105] Anionic surfactant a-2:

A reaction vessel was charged with 437.91 g of ion-

exchanged water and 18.17 g of 48% potassium hydroxide solution, and the mixture was heated to 40°C. Then, 43.92 g of oleic acid (reagent, manufactured by Tokyo Kasei Kogyo Co., Ltd.) was added thereto with stirring. After thorough stirring, the mixture was aged for 1 hour. Thus, a 10% aqueous solution of potassium oleate (anionic surfactant a-2) was obtained.

[0106] Anionic surfactants a-3 and a-4:

The anionic surfactants a-3 and a-4 were synthesized in the same manner as the anionic surfactant a-2, except that the type and the preparation ratio of the compound used (raw fatty acid and alkali used for neutralization) were changed.

[0107] Anionic surfactant a-5:

A reaction vessel was charged with 221.44 g of 1-octanol (reagent, manufactured by Tokyo Kasei Kogyo Co., Ltd.) and dehydrated at 120°C for 2 hours under 0.05 MPa. The pressure was then returned to atmospheric pressure and 78.56 g of diphosphorus pentoxide was added at $60 \pm 5^\circ\text{C}$ for 0.5 hours while stirring. After being aged at 80°C for 3 hours, the mixture was added with 200.0 g of ion-exchanged water and aged for 0.5 hours to obtain a 60% aqueous solution of phosphate ester (a-5), which is an anionic surfactant a-5.

[0108] Anionic surfactant a-6-1:

A reaction vessel was charged with 407.11 g of ion-exchanged water and 71.29 g of a 60% aqueous solution of phosphate ester (a-5), and the mixture was heated to 50°C. Then, 21.61 g of 48% potassium hydroxide solution was added

dropwise thereto to neutralize to obtain a 10% aqueous solution of phosphate ester (a-6-1), which is an anionic surfactant a-6-1.

[0109] Anionic surfactant a-6-2:

A reaction vessel was charged with 136.53 g of 1-octanol (reagent, manufactured by Tokyo Kasei Kogyo Co., Ltd.) and dehydrated at 120°C for 2 hours under 0.05 MPa, the pressure was returned to atmospheric pressure, and 86.93 g of diphosphorus pentoxide was added at 60 ± 5°C for 0.5 hours while stirring. After being aged at 80°C for 3 hours, the mixture was added with 47.74 g of ion-exchanged water and aged for 0.5 hours. To the mixture, 228.81 g of 48% potassium hydroxide solution was added dropwise at 50°C to neutralize to obtain a 60% aqueous solution of phosphate ester (a-6-2). The solution was then adjusted to 10% with ion-exchanged water to obtain a 10% aqueous solution of the anionic surfactant a-6-2.

[0110] Anionic surfactant a-7:

The anionic surfactant a-7 was synthesized in the same manner as the anionic surfactant a-5, except that the type of the compound (raw material alcohol) used and the preparation ratio of raw material alcohol and diphosphorus pentoxide were changed.

[0111] Anionic surfactant a-8:

(Synthesis of Poly(5-mol) oxyethylene octyl ether)

In a pressure vessel equipped with a stirrer, pressure

gauge, and thermometer, 371.58 g of 1-octanol (reagent, manufactured by Tokyo Kasei Kogyo Co., Ltd.) and 1.0 g of potassium hydroxide were charged. Then, while maintaining the reaction system at $150 \pm 5^\circ\text{C}$, 628.42 g of ethylene oxide was added at a gauge pressure of 0.4 MPa for 4 hours, and the temperature of $150 \pm 5^\circ\text{C}$ was maintained for 1 hour, thereby terminating the reaction. The mixture was then neutralized using "KYOWAAD 600 (manufactured by Kyowa Chemical Industry Co., Ltd.)" and filtered to obtain poly(5-mol) oxyethylene octyl ether.

[0112] (Phosphorylation)

Next, 210.96 g of the obtained poly(5-mol) oxyethylene octyl ether was charged to another reaction vessel and dehydrated at 120°C for 2 hours under 0.05 MPa, the pressure was returned to atmospheric pressure, and 47.35 g of diphosphorus pentoxide was added at $60 \pm 5^\circ\text{C}$ for 0.5 hours while stirring. After being aged at 80°C for 3 hours, the mixture was added with 117.06 g of ion-exchanged water and aged for 0.5 hours. To the mixture, 124.63 g of 48% aqueous potassium hydroxide solution was added dropwise at 50°C to neutralize to obtain a 60% aqueous solution of phosphate ester (a-8). The solution was then adjusted to 10% with ion-exchanged water to obtain a 10% aqueous solution of anionic surfactant a-8.

[0113] Anionic surfactant a-9:

The anionic surfactant a-9 was synthesized in the same

manner as the anionic surfactant a-6-1, except that the type of the compound (raw material alcohol) used and the preparation ratio of the raw material alcohol and diphosphorus pentoxide were changed.

[0114] Anionic surfactant a-10:

A reaction vessel was charged with 298.6 g of ion-exchanged water and 90.3 g of 48% potassium hydroxide solution and dissolved uniformly with stirring, and the temperature of the reaction system was maintained at 40°C in a hot water bath. Next, 111.1 g of dodecenyl succinic anhydride (reagent, branched isomer mixture, manufactured by Tokyo Kasei Kogyo Co., Ltd.) was added dropwise over 1 hour to neutralize, then the mixture was stirred at 45°C for 2 hours. After the neutralization reaction, 913.09 g of ion-exchanged water was added and stirred thoroughly. Thus, a 10% aqueous solution of the anionic surfactant a-10 was obtained.

[0115] Anionic surfactant a-11:

The anionic surfactant a-11 was synthesized in the same manner as the anionic surfactant a-10, except as shown in Table 1.

[0116] Anionic surfactant a-12:

A reaction vessel was charged with 701.7 g of ion-exchanged water and 76.3 g of 48% potassium hydroxide solution, and the mixture was heated to 90°C. Then 222.0 g of rosin (reagent, manufactured by Fujifilm Wako Pure Chemical Corporation) was added with stirring. After the addition, the

mixture was aged for 1 hour to obtain a 25% aqueous solution of potassium rosin salt, which is an anionic surfactant a-12.

[0117] (Mass average molecular weight)

The mass average molecular weight of each anionic surfactant (a-1 to a-18) is shown in the column of "Molecular weight" in Table 2. The mass average molecular weight was measured by gel permeation chromatography (GPC) under the following conditions.

<Measurement Conditions>

Equipment: Shodex GPC-101 (manufactured by Showa Denko K.K.)

Column: OHpak SB-G + SB-804M HQ + SB-802.5M HQ (Showa Denko K.K.)

Detector: Differential refractometer (RI)

Eluent: 50mM sodium nitrate aqueous solution

Flow rate: 0.7 mL/min

Column temperature: 40°C

Sample concentration: Eluent solution with sample concentration of 0.5% by mass.

Standard material: PEG/PEO (manufactured by Agilent Technologies, Inc.)

[0118] (P-nuclear NMR integral ratio)

Each anionic surfactant a-5 to a-9 shown in Table 2 is a mixture of the compounds represented by the general formulas (1-3) to (1-5). Therefore, P-nuclear NMR integral ratios attributed to each of the compounds represented by the general formulas (1-3) to (1-5) were measured. The results are shown

in Table 2. In "P-nuclear NMR integral ratio" in Table 2, "mono" indicates the P-nuclear NMR integral ratio attributed to the compound represented by the general formula (1-3), "di" indicates the P-nuclear NMR integral ratio attributed to the compound represented by the general formula (1-4), and "poly" indicates the P-nuclear NMR integral ratio attributed to the compound represented by the general formula (1-5).

[0119] For the P-nuclear NMR integration ratio, first, excess KOH was added to each prepared phosphate ester (organic phosphate ester) to adjust the pH to 12 or higher. Next, ^{31}P -NMR measurement was performed under these conditions (that is, conditions in which an alkaline excess-neutralization pretreatment with KOH has been carried out), and a P-nuclear NMR integral ratio can be calculated based on the following equations (a) to (c) using the obtained measurement values. The ^{31}P -NMR is specifically a MERCURY plus NMR Spectrometer System (300 MHz), which is a product manufactured by Varian, Inc. The solvent used in the ^{31}P -NMR measurement was a mixed solvent of heavy water/tetrahydrofuran = 8/2 (volume ratio).

[0120]

[Equation 4]

$$\begin{array}{l} \text{P-nuclear NMR integral ratio (\%)} \\ \text{of Compound (phosphate ester)} \\ \text{represented by general formula} \\ \text{(1-3)} \end{array} = \frac{\text{P-formula 1}}{(\text{P-formula 1} + \text{P-formula 2} + \text{P-formula 3})} \times 100 \quad (\text{a})$$

[0121]

[Equation 5]

$$\begin{array}{l} \text{P-nuclear NMR integral ratio (\%)} \\ \text{of Compound (phosphate ester)} \\ \text{represented by general formula} \\ \text{(1-4)} \end{array} = \frac{\text{P-formula 2}}{(\text{P-formula 1} + \text{P-formula 2} + \text{P-formula 3})} \times 100 \quad (\text{b})$$

[0122]

[Equation 6]

$$\begin{array}{l} \text{P-nuclear NMR integral ratio (\%)} \\ \text{of Compound (phosphate ester)} \\ \text{represented by general formula} \\ \text{(1-5)} \end{array} = \frac{\text{P-formula 3}}{(\text{P-formula 1} + \text{P-formula 2} + \text{P-formula 3})} \times 100 \quad (\text{c})$$

[0123] In the above equations (a) to (c), P-formula 1, P-formula 2, and P-formula 3 are as follows.

P-formula 1: P-nuclear NMR integral value attributed to the compound (phosphate ester) represented by the general formula (1-3).

P-formula 2: P-nuclear NMR integral value attributed to the compound (phosphate ester) represented by the general formula (1-4).

P-formula 3: P-nuclear NMR integral value attributed to the compound (phosphate ester) represented by the general formula (1-5).

[0124] (2) Hydraulic composition:

Next, a hydraulic composition (mortar) was prepared by employing Formulations C-1 to C-3 shown in Table 3.

[0125] Specifically, first, ordinary Portland cement, blast furnace slag fine powder #4000, a carbonation admixture LEAF mainly composed of γ -2CaO $\cdot$ SiO₂, fine aggregate, carbon dioxide (CO₂)-fixed fine powder (CCU fine powder), and carbon

dioxide (CO₂)-fixed modified recycled aggregate (CCU recycled fine aggregate) were sequentially charged into a mixer specified in JIS R5201 according to Formulations C-1 to C-3 (mortar formulation) as shown in Table 3, and then dry mixed for 10 seconds. In this case, ordinary Portland cement, blast furnace slag fine powder, and the carbonation admixture were regarded as binders. Ordinary Portland cement has a density of 3.16 g/cm³ (manufactured by Taiheiyo Cement Corporation). Blast furnace slag fine powder #4000 has a density of 2.89g/cm³ (Esment). The carbonation admixture LEAF mainly composed of γ -2CaO·SiO₂ has a density of 3.09g/cm³ (manufactured by Denka Company Limited). The fine aggregate has a density of 2.58 g/cm³ (Oigawa River system land sand). The carbon dioxide (CO₂)-fixed fine powder has a density of 2.51 g/cm³. The carbon dioxide (CO₂)-fixed modified recycled aggregate has a density of 2.42 g/cm³.

[0126] The following are specific examples of CO₂-fixed fine powder and CO₂-fixed modified recycled aggregate.

[0127] The CO₂-fixed fine powder contains modified concrete powder, which has a 50% particle size of 50μm or less and is a reaction product of recycled concrete powder and carbon dioxide gas, and contains calcium carbonate and a siliceous material.

[0128] The CO₂-fixed fine powder was specifically produced as follows. That is, a concrete mass was crushed and grinded by a known crusher to obtain recycled concrete fine powder

with a median diameter of 100 μ m or less. Then, 1800 kg of water and 200 kg of the obtained recycled concrete fine powder were sequentially charged into a 2m³ capacity vessel and stirred. Furthermore, carbon dioxide gas was injected from the bottom of the vessel at a rate of 150L/min to react the recycled concrete fine powder with CO₂. The above reaction process was continued until the pH of the dispersion liquid was below 6.8, and a reaction product of recycled concrete fine powder and CO₂ was obtained. After the reaction was completed, the obtained reaction product was taken out, excess water was removed with a twill-woven polypropylene filter, and the product was air-dried to obtain CO₂-fixed fine powder.

[0129] The CO₂-fixed modified recycled aggregate (specifically, the CO₂-fixed modified recycled fine aggregate) includes modified recycled fine aggregate, which is a dry or wet reaction product of recycled fine aggregate with water absorption of greater than 3.0% and 10% or less and carbon dioxide gas, and contains calcium carbonate, silicon dioxide and gypsum.

[0130] The CO₂-fixed modified recycled aggregate was specifically produced as follows. That is, a concrete mass was crushed and grinded by a known crusher, and then classified by a sieve so that all particles had a particle size of 10mm or less, and the particles with water absorption greater than 3% and 10% or less were obtained as recycled fine aggregate. Then, 1800 kg of water and 200 kg of the obtained recycled fine

aggregate were sequentially charged into a 2m³ capacity vessel and stirred. Furthermore, carbon dioxide gas was injected from the bottom of the vessel at a rate of 150 L/min to react the recycled fine aggregate with CO₂. The above reaction process was continued until the pH of the dispersion liquid was below 6.8, and a reaction product of recycled fine aggregate and CO₂ was obtained. After the reaction was completed, the obtained reaction product was taken out, excess water was removed with a twill-woven polypropylene filter, and the product was air-dried to obtain CO₂-fixed modified recycled fine aggregate.

[0131] Next, the carbonation accelerator for a hydraulic composition shown in Table 1, a water reducing agent (Chupol NV-80 (trade name), a high-performance water reducing agent manufactured by Takemoto Oil and Fat Co., Ltd.), and a defoaming agent (AFK-2 (trade name) manufactured by Takemoto Oil and Fat Co., Ltd.) were added to the mixing water. However, the above-described carbonation accelerator, water reducing agent, and defoaming agent were regarded as a part of the mixing water. The mixing water was then charged into the mixer and kneaded for 180 seconds to obtain a hydraulic composition (mortar).

[0132] The defoaming agent was added at 0.0005% by mass to the binder (however, no defoaming agent was added in Comparative Examples 2, 5, and 8). The carbonation accelerator for a hydraulic composition was adjusted and added to the binder in the range of 0.001 to 0.05% by mass as shown in

Tables 4 to 6 so that the air content of the kneaded mortar was within 4.5 ± 0.5 %. However, in Comparative Examples 2, 5, and 8, the mixer was agitated at high speed when mixing the mortar so that the air content of the finished mortar was $4.5 \pm 0.5\%$.

[0133] The amount of the water reducing agent added was set to within 200 ± 5 mm of mortar flow for Formulations C-1 and C-2, and to within 275 ± 5 mm of mortar flow for Formulation C-3.

[0134] [Table 3]

Form ulat ion type	Water/ binder (%)	Water/ powder (%)	Fine aggrega te/ binder	Fine aggreg ate/ powder	Amount of each component (upper row: kg/m ³ , lower row: L/m ³)										Amount of material- derived CO ₂ emission (α) (kg/m ³)
					Water	Powder				Oigawa River system land sand	CCU recycled fine aggregate	Total			
						Binder		Carbonation admixture	CCU fine powder						
						Ordinary Portland cement	Blast furnace slag fine powder								
C-1	55.0	55.0	1.78	1.78	342	187	435	0	0	1105	0	2069	154.2		
					342	59	151	0	0	428	0	980			
C-2	55.0	55.0	1.78	1.78	343	131	306	187	0	1108	0	2074	131.5		
					343	41	106	61	0	429	0	980			
C-3	55.0	36.7	1.28	0.85	335	128	298	183	304	0	777	2025	82.0		
					335	40	103	59	121	0	321	980			

[0135] Formulations C-1 to C-3 have the following relationships. Specifically, no carbonation admixture was used in Formulation C-1, while the carbonation admixture was used in Formulations C-2 and C-3. The carbonation admixture is 30% by mass on an internal basis with respect to the binder. Formulation C-3 contains CCU fine powder, and the CCU fine powder is one in which fine aggregate is replaced at 50% by mass on an external basis with respect to the binder. In addition, Formulation C-3 contains CCU recycled fine aggregate, and 100% of the fine aggregate was replaced by the CCU recycled fine aggregate.

[0136] In Table 3, "Amount of material-derived CO₂ emission (α)" was calculated based on the amount of carbon dioxide emitted during the production of each component. That is, the amount of carbon dioxide emission of ordinary Portland is 764.3 kg/t, and the amount of carbon dioxide emission of blast furnace slag fine powder is 26.5 kg/t. Then, the amount of carbon dioxide emission of carbonation admixture is 124.5 kg/t, the amount of carbon dioxide emission of CCU recycled fine aggregate is -26.9 kg/t, and the amount of carbon dioxide emission of CCU fine powder is -83.8 kg/t.

[0137] Tables 4 to 6 show the test results (mortar flow (mm), air content (%)) for mortars prepared by employing Formulations C-1 to C-3, respectively, and other results such as carbon dioxide balance. Note that the values in "Amount of material-derived CO₂ emission (α)" in Tables 4 to 6 are the

"Amount of material-derived CO₂ emission (α)" shown in Table 3.

[0138] In Examples 1 to 16 and Comparative Examples 1 and 2 shown in Table 4, the values for "Amount of carbon dioxide reduction" by the carbonation accelerator for a hydraulic composition are obtained by calculating the difference between the carbon dioxide balance of each Example and Comparative Example and the carbon dioxide balance of Comparative Example 3 as a reference. In Examples 17 to 32 and Comparative Examples 5 and 6 shown in Table 5, the values for "Amount of carbon dioxide reduction" by the carbonation accelerator for a hydraulic composition are obtained by calculating the difference between the carbon dioxide balance of each Example and Comparative Example and the carbon dioxide balance of Comparative Example 7 as a reference. In Examples 33 to 48 and Comparative Examples 9 and 10 shown in Table 6, the values for "Amount of carbon dioxide reduction" by the carbonation accelerator for a hydraulic composition are obtained by calculating the difference between the carbon dioxide balance of each Example and Comparative Example and the carbon dioxide balance of Comparative Example 11 as a reference.

[0139] In Comparative Examples 3, 7, and 11, only a water reducing agent is used without using a carbonation accelerator for a hydraulic composition. In Comparative Examples 3, 7, and 11, air is intentionally entrained within the hydraulic composition by stirring the hydraulic composition at high speed. However, the air entrained is coarser than that in the case

where a carbonation accelerator for a hydraulic composition is used. Since the carbon dioxide balances of Comparative Examples 4, 8, and 12 are greater than those of Comparative Examples 3, 7, and 11, respectively, the "Amount of carbon dioxide reduction" was not calculated.

[0140] Measurement methods for mortar flow (mm) and air content (%) of the hydraulic composition are shown below.

[0141] (Mortar flow)

The hydraulic composition immediately after mixing was measured in accordance with JIS R5201 in a state without a falling motion.

[0142] (Air volume (% by volume))

The hydraulic composition immediately after mixing was measured in accordance with JIS A1116 using a container for mortar.

[0143] (3) Method for manufacturing hydraulic composition hardened body:

(Hardening step of Mortar)

First, a cylindrical tin-plate concrete specimen molding formwork (product name "Summit Mold", manufactured by S. C. Cement Co., Ltd, diameter of the bottom of the formwork 50 mm, height of the formwork 100 mm) was prepared, and the formwork was filled with the prepared hydraulic composition (mortar) using the two-layer filling method.

[0144] Next, air curing (20°C) was performed in a room at 20°C. Two hours after the mortar was prepared, the surface of

the filled mortar was leveled, covered with polyethylene wrap to prevent moisture from evaporating, and sealed and cured for two days of the material age. A specimen (mortar hardened body) was then obtained.

[0145] (Carbonation curing step of Mortar hardened body (hydraulic composition hardened body))

After sealing and curing, the specimen (mortar hardened body) was removed from the framework and carbonation curing was performed until a material age of 7 days (curing conditions: 20°C, 60% RH, and a carbon dioxide volume concentration of 60%) in a high concentration accelerated carbonation curing chamber (manufactured by MARUI & Co., Ltd.) capable of controlling temperature, humidity, and carbon dioxide concentration. At this time, carbonation was carried out from the entire surface of the specimen without covering the specimen. The hydraulic composition hardened body was manufactured in this way.

[0146] (Measurement of CO₂ fixation amount)

For the manufactured hydraulic composition hardened body, the amount of carbon dioxide fixed therein was measured as follows.

[0147] (Method of preparing sample for analysis)

After carbonation curing, the specimen (hydraulic composition hardened body) was removed from the curing chamber and promptly moved to a furnace at 105°C for drying treatment for 2 days. After drying, the specimen was entirely crushed

and further pulverized with a ball mill to 150 μ m or less, and used as a sample for analysis.

[0148] (Methods for Measuring total carbon content and Calculating CO₂ fixation amount by carbonation curing)

To confirm the amount of carbon dioxide fixed by carbonation curing (amount of CO₂ fixation), the total carbon content (C (%)) in the sample for analysis was measured using Total Organic Carbon Analyzer ("TOC-L" and Solid Sample Combustion Unit "SSM-5000A" manufactured by Shimadzu Corporation). The measurement conditions were such that the sample amount was 50 mg and the combustion temperature was 900°C.

[0149] From the obtained total carbon content, the amount of CO₂ fixed in the sample for analysis (%) was calculated using the following formula, and the amount of carbon dioxide fixed by carbonation curing (kg-CO₂/m³) was determined.

Formula: CO₂ (%) = C (%) $\times$ 44/12

[0150] The amount of CO₂ fixation is a percentage of the sample weight after heat treatment at 900°C. The amount of CO₂ fixation by carbonation curing is calculated by subtracting the amount of carbon detected as derived from the materials used in the mortar and the components added (water reducing agent, defoaming agent, and carbonation accelerator for a hydraulic composition). The above "materials used in the mortar" are cement, blast furnace slag fine powder, carbonation accelerator, CO₂-fixed fine powder, fine aggregate, and CO₂-

fixed modified recycled aggregate (CO₂-fixed modified recycled fine aggregate).

[0151] In Tables 4 to 6, "Carbon dioxide balance (α - β)" is the value calculated by the equation: Amount of material-derived CO₂ emissions (α) - Amount of CO₂ fixed by carbonation curing (β). The "Amount of carbon dioxide reduction" is a value calculated by the equation: |"Carbon dioxide balance" in each Example - "Carbon dioxide balance" of Comparative Examples 3, 7, and 11|. The results of the "Amount of carbon dioxide reduction" indicate that each Example exhibits a superior carbon dioxide absorption effect as compared with the reference Comparative Examples 3, 7, and 11. That is, in each Example, the carbonation of the hydraulic composition is accelerated by the carbonation accelerator for a hydraulic composition.

[0152] [Table 4]

Examples/ Comparative Examples	Form ulation type	Water reducing agent		Carbonation accelerator for a hydraulic composition		Mortar flow (mm)	Air content (%)	Amount of material- derived CO ₂ emission (α) (kg-CO ₂ /m ³)	Amount of CO ₂ fixed by carbonation curing (β) (kg-CO ₂ /m ³)	Carbon dioxide balance (α-β) (kg- CO ₂ /m ³)	Amount of carbon dioxide reduction *1	
		Type	Bx% (as-is)	Type	Bx% (as-is)						(kg-CO ₂ /m ³)	Evaluation
Example 1	C-1	Chupol NV-80	0.40	A-1	0.0020	203	4.8	154.2	126.0	28.2	32.3	S
Example 2	C-1		0.40	A-2	0.0035	199	4.4	154.2	127.4	26.8	33.7	S
Example 3	C-1		0.40	A-3	0.0040	195	4.8	154.2	125.5	28.7	31.8	S
Example 4	C-1		0.40	A-4	0.0045	199	4.1	154.2	130.0	24.2	36.3	S
Example 5	C-1		0.40	A-5	0.0030	199	4.7	154.2	126.9	27.3	33.2	S
Example 6	C-1		0.40	A-6	0.0035	201	4.2	154.2	131.0	23.2	37.3	S
Example 7	C-1		0.40	A-7	0.0030	197	4.9	154.2	125.6	28.6	31.9	S
Example 8	C-1		0.40	A-8	0.0020	203	4.8	154.2	126.3	27.9	32.6	S
Example 9	C-1		0.40	A-9	0.0040	200	4.3	154.2	129.3	24.9	35.6	S
Example 10	C-1		0.40	A-10	0.0030	196	4.8	154.2	127.5	26.7	33.8	S
Example 11	C-1		0.40	A-11	0.0020	196	4.6	154.2	130.9	23.3	37.2	S
Example 12	C-1		0.40	A-12	0.0045	202	4.6	154.2	119.1	35.1	25.4	A
Example 13	C-1		0.40	A-13	0.0040	199	4.4	154.2	120.1	34.1	26.4	A
Example 14	C-1		0.40	A-14	0.0035	197	4.4	154.2	107.4	46.8	13.7	B
Example 15	C-1		0.40	A-15	0.0025	200	4.2	154.2	106.8	47.4	13.1	B
Example 16	C-1		0.40	A-16	0.0030	202	4.5	154.2	107.6	46.6	13.9	B
Comparative Example 1	C-1		0.40	RA-1	0.0025	196	4.6	154.2	95.1	59.1	1.4	C
Comparative Example 2	C-1		0.36	RA-2	0.0800	196	4.4	154.2	94.8	59.4	1.1	C
Comparative Example 3	C-1		0.40	-	-	195	4.5	154.2	93.7	60.5	0.0	C
Comparative Example 4	C-1		0.40	-	-	203	1.2	154.2	93.3	60.9	-	-

*1: a value calculated by the equation: |"Carbon dioxide balance" in each Example - "Carbon dioxide balance" of Comparative Example 3|.

[0153] In Table 4, the following evaluation criteria were used for "Amount of carbon dioxide reduction".

S: Amount of carbon dioxide reduction (kg-CO₂/m³) is 30kg-CO₂/m³

or more

A: Amount of carbon dioxide reduction ($\text{kg-CO}_2/\text{m}^3$) is $20\text{kg-CO}_2/\text{m}^3$
or more and less than $30\text{kg-CO}_2/\text{m}^3$

B: Amount of carbon dioxide reduction ($\text{kg-CO}_2/\text{m}^3$) is $10\text{kg-CO}_2/\text{m}^3$
or more and less than $20\text{kg-CO}_2/\text{m}^3$

C: Amount of carbon dioxide reduction ($\text{kg-CO}_2/\text{m}^3$) is less than
 $10\text{kg-CO}_2/\text{m}^3$

[0154] [Table 5]

Examples/ Comparative Examples	Form ulation type	Water reducing agent		Carbonation accelerator for a hydraulic composition		Mortar flow (mm)	Air content (%)	Amount of material- derived CO ₂ emission (α) (kg-CO ₂ /m ³)	Amount of CO ₂ fixed by carbonation curing (β) (kg-CO ₂ /m ³)	Carbon dioxide balance (α-β) (kg- CO ₂ /m ³)	Amount of carbon dioxide reduction *1	
		Type	B×% (as- is)	Type	B×% (as-is)						(kg-CO ₂ /m ³)	Eval uation
Example 17	C-2	Chupol NV-80	0.52	A-1	0.0035	202	4.7	131.5	145.6	-14.1	30.5	S
Example 18	C-2		0.52	A-2	0.0025	205	4.3	131.5	146.6	-15.1	31.5	S
Example 19	C-2		0.52	A-3	0.0040	201	4.8	131.5	145.1	-13.6	30.0	S
Example 20	C-2		0.52	A-4	0.0020	205	4.8	131.5	149.3	-17.8	34.2	S
Example 21	C-2		0.52	A-5	0.0040	205	4.1	131.5	147.7	-16.2	32.6	S
Example 22	C-2		0.52	A-6	0.0020	199	4.8	131.5	147.5	-16.0	32.4	S
Example 23	C-2		0.52	A-7	0.0030	203	4.6	131.5	146.6	-15.1	31.5	S
Example 24	C-2		0.52	A-8	0.0045	198	4.7	131.5	145.2	-13.7	30.1	S
Example 25	C-2	Chupol NV-80	0.52	A-9	0.0030	204	4.5	131.5	149.5	-18.0	34.4	S
Example 26	C-2		0.52	A-10	0.0035	204	4.6	131.5	147.2	-15.7	32.1	S
Example 27	C-2		0.52	A-11	0.0035	205	4.2	131.5	149.1	-17.6	34.0	S
Example 28	C-2		0.52	A-12	0.0040	199	4.6	131.5	137.9	-6.4	22.8	A
Example 29	C-2		0.52	A-13	0.0040	205	4.9	131.5	137.2	-5.7	22.1	A
Example 30	C-2		0.52	A-14	0.0045	199	4.2	131.5	127.9	3.6	12.8	B
Example 31	C-2		0.52	A-15	0.0035	198	4.6	131.5	128.9	2.6	13.8	B
Example 32	C-2		0.52	A-16	0.0025	199	4.4	131.5	129.9	1.6	14.8	B
Comparative Example 5	C-2	Chupol NV-80	0.52	RA-1	0.0040	201	4.4	131.5	118.4	13.1	3.3	C
Comparative Example 6	C-2		0.47	RA-2	0.1000	200	4.5	131.5	117.2	14.3	2.1	C
Comparative Example 7	C-2		0.52	-	-	197	4.5	131.5	115.1	16.4	0.0	C
Comparative Example 8	C-2		0.52	-	-	200	1.1	131.5	115.4	16.1	-	-

*1: a value calculated by the equation: |"Carbon dioxide balance" in each Example - "Carbon dioxide balance" of Comparative Example 7|.

[0155] In Table 5, the following evaluation criteria were used for the "amount of carbon dioxide reduction".

S: Amount of carbon dioxide reduction ($\text{kg-CO}_2/\text{m}^3$) is $30\text{kg-CO}_2/\text{m}^3$ or more

A: Amount of carbon dioxide reduction ($\text{kg-CO}_2/\text{m}^3$) is $20\text{kg-CO}_2/\text{m}^3$ or more and less than $30\text{kg-CO}_2/\text{m}^3$

B: Amount of carbon dioxide reduction ($\text{kg-CO}_2/\text{m}^3$) is $10\text{kg-CO}_2/\text{m}^3$ or more and less than $20\text{kg-CO}_2/\text{m}^3$

C: Amount of carbon dioxide reduction ($\text{kg-CO}_2/\text{m}^3$) is less than $10\text{kg-CO}_2/\text{m}^3$

[0156] [Table 6]

Examples/ Comparative Examples	Form ulation type	Water reducing agent		Carbonation accelerator for a hydraulic composition		Mortar flow (mm)	Air content (%)	Amount of material- derived CO ₂ emission (α) (kg-CO ₂ /m ³)	Amount of CO ₂ fixed by carbonation curing (β) (kg-CO ₂ /m ³)	Carbon dioxide balance ($\alpha-\beta$) (kg- CO ₂ /m ³)	Amount of carbon dioxide reduction *1	
		Type	B% (as- is)	Type	B% (as-is)						(kg-CO ₂ /m ³)	Evaluation
Example 33	C-3	Chupol NV-80	1.20	A-1	0.008	280	4.9	82.0	97.3	-15.3	28.9	S
Example 34	C-3		1.20	A-2	0.006	280	4.1	82.0	100.1	-18.1	31.7	S
Example 35	C-3		1.20	A-3	0.007	280	4.4	82.0	98.3	-16.3	29.9	S
Example 36	C-3		1.20	A-4	0.007	278	5.0	82.0	100.8	-18.8	32.4	S
Example 37	C-3		1.20	A-5	0.005	276	4.8	82.0	95.8	-13.8	27.4	S
Example 38	C-3		1.20	A-6	0.008	275	4.5	82.0	98.8	-16.8	30.4	S
Example 39	C-3		1.20	A-7	0.005	276	4.2	82.0	97.1	-15.1	28.7	S
Example 40	C-3		1.20	A-8	0.009	270	4.9	82.0	97.2	-15.2	28.8	S
Example 41	C-3		1.20	A-9	0.007	274	4.1	82.0	99.3	-17.3	30.9	S
Example 42	C-3		1.20	A-10	0.008	270	4.7	82.0	95.1	-13.1	26.7	S
Example 43	C-3		1.20	A-11	0.007	272	4.6	82.0	97.4	-15.4	29.0	S
Example 44	C-3		1.20	A-12	0.005	279	5.0	82.0	90.3	-8.3	21.9	A
Example 45	C-3		1.20	A-13	0.008	270	4.5	82.0	90.4	-8.4	22.0	A
Example 46	C-3		1.20	A-14	0.010	274	4.9	82.0	79.8	2.2	11.4	B
Example 47	C-3		1.20	A-15	0.005	275	4.6	82.0	79.2	2.8	10.8	B
Example 48	C-3		1.20	A-16	0.005	276	4.8	82.0	78.4	3.6	10.0	B
Comparative Example 9	C-3		1.20	RA-1	0.010	270	4.3	82.0	69.8	12.2	1.4	C
Comparative Example 10	C-3		1.08	RA-2	0.240	271	4.4	82.0	69.5	12.5	1.1	C
Comparative Example 11	C-3		1.20	-	-	270	4.8	82.0	68.4	13.6	0.0	C
Comparative Example 12	C-3		1.20	-	-	273	1.2	82.0	65.2	16.8	-	-

*1: a value calculated by the equation: |"Carbon dioxide balance" in each Example - "Carbon dioxide balance" of Comparative Example 11|.

[0157] In Table 6, the following evaluation criteria were used for the "amount of carbon dioxide reduction".

S: Amount of carbon dioxide reduction (kg-CO₂/m³) is 25kg-CO₂/m³

or more

A: Amount of carbon dioxide reduction ($\text{kg-CO}_2/\text{m}^3$) is $20\text{kg-CO}_2/\text{m}^3$ or more and less than $25\text{kg-CO}_2/\text{m}^3$

B: Amount of carbon dioxide reduction ($\text{kg-CO}_2/\text{m}^3$) is $10\text{kg-CO}_2/\text{m}^3$ or more and less than $20\text{kg-CO}_2/\text{m}^3$

C: Amount of carbon dioxide reduction ($\text{kg-CO}_2/\text{m}^3$) is less than $10\text{kg-CO}_2/\text{m}^3$

[0158] (Result)

As shown in Tables 4 to 6, it can be seen that the addition of the carbonation accelerator for a hydraulic composition in Examples accelerates carbonation of the hydraulic composition and increases the amount of carbon dioxide reduction by the hydraulic composition (hydraulic composition hardened body). In addition, according to the method for manufacturing a hydraulic composition hardened body in Examples, it is possible to accelerate carbonation of the hydraulic composition and increase the amount of carbon dioxide absorbed by the hydraulic composition hardened body to be manufactured (the amount of carbon dioxide reduction) by using the carbonation accelerator for a hydraulic composition in Examples as a raw material.

Industrial Availability

[0159] The carbonation accelerator for a hydraulic composition of the present invention can be used as a raw material for a hydraulic composition hardened body that reduces

carbon dioxide by adding it to a hydraulic composition. The method for manufacturing a hydraulic composition hardened body of the present invention can be employed as a manufacturing method of a hydraulic composition hardened body that absorbs carbon dioxide.

CLAIMS

1. A carbonation accelerator for a hydraulic composition comprising an anionic surfactant at a ratio of 10 to 100% by mass, wherein the anionic surfactant is a compound containing an organic acid ion with a hydrophobic group having 6 to 50 carbon atoms in the molecule.

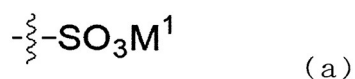
2. The carbonation accelerator for a hydraulic composition according to claim 1, wherein the anionic surfactant is at least one compound selected from the compounds represented by the following general formula (1).

[Formula 1]

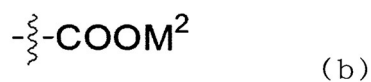


(In the general formula (1), R^1 is an alkyl group having 1 to 24 carbon atoms, an alkenyl group having 2 to 24 carbon atoms, an aryl group having 8 to 20 carbon atoms, a residue obtained by removing a carboxylic acid from rosin, or a residue obtained by removing hydrogen from an adduct formed by adding a total of 1 to 10 moles of an alkylene oxide having 2 to 3 carbon atoms to 1 mole of an aliphatic alcohol having 1 to 24 carbon atoms. X is represented by the following general formulas (a) to (f).)

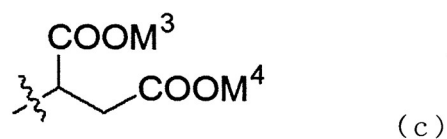
[Formula 2]



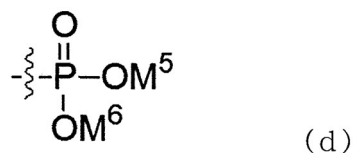
[Formula 3]



[Formula 4]



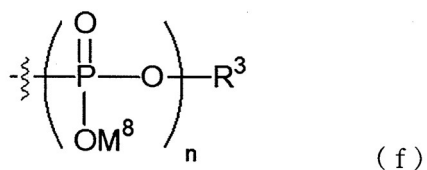
[Formula 5]



[Formula 6]



[Formula 7]

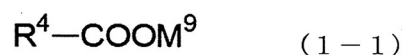


(In the general formulas (a) to (f), R^2 and R^3 are each independently a residue obtained by removing a hydroxyl group from an aliphatic alcohol having 1 to 24 carbon atoms, or a residue obtained by removing a hydroxyl group from an adduct formed by adding a total of 1 to 10 moles of an alkylene oxide having 2 to 3 carbon atoms to 1 mole of an aliphatic alcohol

having 1 to 24 carbon atoms. M^1 to M^8 are each independently an alkali metal, an alkaline earth metal, ammonium, or an organic amine. n is an integer of 2 or 3.)

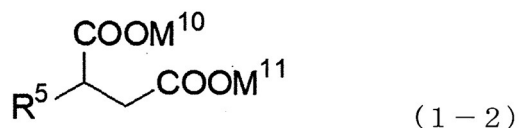
3. The carbonation accelerator for a hydraulic composition according to claim 1, wherein the anionic surfactant is at least one selected from the compounds represented by the following general formulas (1-1) to (1-5).

[Formula 8]



(In the general formula (1-1), R^4 is an alkyl group having 6 to 20 carbon atoms, an alkenyl group having 6 to 20 carbon atoms, or an acyl residue of rosin. M^9 is hydrogen, an alkali metal, an alkaline earth metal, ammonium, or an organic amine.)

[Formula 9]



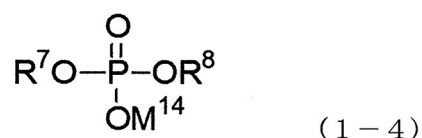
(In the general formula (1-2), R^5 is an alkyl group having 6 to 20 carbon atoms, an alkenyl group having 6 to 20 carbon atoms, or an aryl group having 6 to 20 carbon atoms. M^{10} to M^{11} are hydrogen, an alkali metal, an alkaline earth metal, ammonium, or an organic amine.)

[Formula 10]



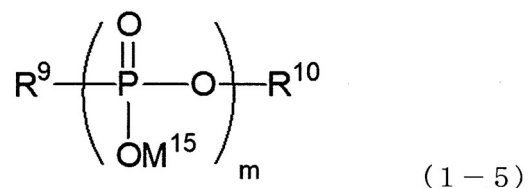
(In the general formula (1-3), R^6 is a residue obtained by removing a hydroxyl group from an aliphatic alcohol having 6 to 20 carbon atoms, or a residue obtained by removing a hydroxyl group from an adduct formed by adding a total of 1 to 10 moles of an alkylene oxide having 2 to 3 carbon atoms to 1 mole of an aliphatic alcohol having 6 to 20 carbon atoms. M^{12} and M^{13} are each independently hydrogen, an alkali metal, an alkaline earth metal, ammonium or an organic amine.)

[Formula 11]



(In the general formula (1-4), R^7 and R^8 are each independently a residue obtained by removing a hydroxyl group from an aliphatic alcohol having 6 to 20 carbon atoms, or a residue obtained by removing a hydroxyl group from an adduct formed by adding a total of 1 to 10 moles of an alkylene oxide having 2 to 3 carbon atoms to 1 mole of an aliphatic alcohol having 6 to 20 carbon atoms. M^{14} is hydrogen, an alkali metal, an alkaline earth metal, ammonium or an organic amine.)

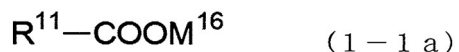
[Formula 12]



(In the general formula (1-5), R⁹ and R¹⁰ are each independently a residue obtained by removing a hydroxyl group from an aliphatic alcohol having 6 to 20 carbon atoms, or a residue obtained by removing a hydroxyl group from an adduct formed by adding a total of 1 to 10 moles of an alkylene oxide having 2 to 3 carbon atoms to 1 mole of an aliphatic alcohol having 6 to 20 carbon atoms. M¹⁵ is hydrogen, an alkali metal, an alkaline earth metal, ammonium or an organic amine. m is an integer of 2 or 3.)

4. The carbonation accelerator for a hydraulic composition according to claim 3, wherein the anionic surfactant is a mixture containing at least one selected from the compound represented by the general formula (1-1a) and the compound represented by the general formulas (1-2) to (1-5).

[Formula 13]



(In the general formula (1-1a), R¹¹ is an alkyl group having 6 to 20 carbon atoms or an alkenyl group having 6 to 20 carbon atoms. M¹⁶ is hydrogen, an alkali metal, an alkaline earth metal, or an organic amine.)

5. The carbonation accelerator for a hydraulic composition

according to any one of claims 1 to 4, which is added to a hydraulic composition that becomes a hydraulic composition hardened body after undergoing a carbonation curing step, which is a step of curing in an environment with a carbon dioxide volume concentration of 5% or more.

6. The carbonation accelerator for a hydraulic composition according to any one of claims 1 to 4, which is added to a hydraulic composition containing a binder that contains blast furnace slag fine powder at 40 to 99% by mass, water, and an aggregate.

7. The carbonation accelerator for a hydraulic composition according to any one of claims 1 to 4, wherein the hydraulic composition contains γ -2CaO·SiO₂.

8. The carbonation accelerator for a hydraulic composition according to any one of claims 1 to 4, wherein the hydraulic composition contains at least one selected from the following CO₂-fixed fine powder and the following CO₂-fixed modified recycled fine aggregate.

CO₂-fixed fine powder:

including modified concrete powder, which has a 50% particle size of 50μm or less and is a reaction product of recycled concrete powder and carbon dioxide gas,

wherein the modified concrete powder contains calcium

carbonate and a siliceous material, and

wherein a content ratio of the CO₂-fixed fine powder in the hydraulic composition is in the range of 1 to 100% by mass with respect to 100% by mass of the binder.

CO₂-fixed modified recycled fine aggregate:

including modified recycled fine aggregate in which all particles have a particle size of 10 mm or less and 85% or more of the particles have a particle size of 5 mm or less, the modified recycled fine aggregate being a dry or wet reaction product of recycled fine aggregate having a water absorption greater than 3.0% and 10% or less and carbon dioxide gas,

wherein the modified recycled fine aggregate contains calcium carbonate and silicon dioxide, and

wherein the content ratio of the CO₂-fixed modified recycled fine aggregate in the hydraulic composition is in the range of 10 to 100% by volume with respect to the total aggregate volume.

9. A method for manufacturing a hydraulic composition hardened body, comprising:

a preparation step of preparing a hydraulic composition containing a carbonation accelerator for a hydraulic composition according to any one of claims 1 to 4, a binder containing blast furnace slag fine powder at 40 to 99% by mass, and water;

a hardening step of hardening the obtained hydraulic composition to obtain a hydraulic composition hardened body;
and

a carbonation curing step of curing the obtained hydraulic composition hardened body in an environment with a carbon dioxide volume concentration of 5% or more to absorb and fix carbon dioxide in the hydraulic composition hardened body.